

STUDIES IN DETERGENTY

by

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STUDIES IN DETERGENCY

INTRODUCTION

Soap solutions are the most efficient, the most economical, and the most widely used cleansing agents known. Water solutions of soaps have relatively low surface tensions, high viscosities, and the power to stabilize suspensions of solids and liquids. When soap is used in the laundry, alkaline builders are nearly always added since it is generally believed that these salts increase the detergent power of the soap. Many workers have made measurements of the physical and chemical properties of soap solutions without satisfactorily establishing any of them as a quantitative measure of detergent power. The work represented by this paper was attempted in an effort to establish some relationship between the surface tension, pH value, and the detergent value of soap solutions when the detergent value is measured by controlled washing tests.

HISTORY OF SOAP

The cleansing action of soap has been known since Biblical times. Feldhaus-Friedenau (1) states that the ancients were familiar with salt, sodium carbonate, honey, bone meal, bran, Lemnian earth, pumice, and decomposed urine as washing materials. He says that the last named product was used mainly for its ammonia content and was almost universally employed by the old Roman laundries. He states that mural paintings were discovered in 1775 at Civitia, Italy, which show an old Roman laundry in one of the scenes and that a well preserved laundry was unearthed in Pompeii in 1826. He states that Pliny, in 190, reports that the first soap was made by the Gauls from goat tallow and wood ashes and was used by them as a hair pomade. He reports that Galenos, in 200 A.D., gave the first mention of the use of soap as a cleansing material. Soap boiling, according to Feldhaus-Friedenau (1), was first authentically mentioned in Germany about 805 under Charlemange. He states that during the Middle Ages, soap was used mainly by the more wealthy people as a cleansing agent for fine fabrics, and that by the seventeenth century, a patent had been issued in England to a band of soap boilers, which resulted in a very large consumption of soap in that country.

Chevreul (2) as a result of his researches on fats and oils explained the chemical constitution of soaps. He stated that soap was the metal salt of long chain fatty acids which were produced by the hydrolysis of fats. Chevreul (2) also gave the first theory of the detergent action of soap solutions.

THEORIES OF DETERGENCY

The first theory as to the cleansing action of soap solutions was that of Chevreul (2) in 1823. He showed that soap, dissolved in water, hydrolysed into free alkali and acid salts of the fatty acids. He assumed that all dirt was covered with a film of fatty substance and as a result of this film, the particles of dirt adhered to surfaces. The free alkali was thought to saponify this film of fatty material, which released the dirt particle, and allowed its suspension in the suds. He assumed that rinsing would wash away and prevent redeposition of the suspended dirt particles. He also believed that the property of foaming and the emulsifying power was due to the undecomposed soap in the solution. This theory of the detergent action was not disproven for almost a century.

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According to Fall (4), with only one or two exceptions, all of the theories of detergent action, up to 1903, were founded on the belief that the alkali of hydrolysis of the soap was the active agent.

Hillyer (5) published an investigation in 1903 which completely disproved the theory that free alkali was responsible for the cleansing action of soap solutions. He showed that the emulsifying power of soap solutions could not be duplicated by concentrated solutions of alkalies and hence, that the emulsifying power of soap solutions could not be attributed to the free alkali produced by the hydrolysis of the soap. He further showed that concentrated solutions of alkali did not have the property of wetting oily material as did soap solutions. Finally, he demonstrated that only solutions with low surface tensions were able to form stable emulsions. He showed that saponin emulsified through the formation of a solid surface film instead of through low surface tension. He concluded that the cleansing action of soap solutions was due to the soap itself and not to any other agents which might be present in the solutions.

In 1909, Spring (5) showed that soap could suspend and carry oil-free lamp black, alumina, iron oxide, and silica, through filter paper. He showed that soap made these particles less adherent to fibers and to each other. He also proved that part of the dirt is free from the surrounding film of oil and that this film was not necessary for detergent action. Spring stated that the attraction of both fabric and dirt for soap exceeds the attraction of the fabric for dirt and of dirt particles for each other.

Salmon (6) has investigated the conductivity of soap solutions and has found very high values for specific conductivity at certain concentrations. It was at first assumed that this conductivity was due to the carrying of current by the NaOH formed by hydrolysis. McBain and Salmon (7) have disproven this explanation by their measurements of the degree of hydrolysis by means of pH determinations. With solutions of sodium palmitate, the ionic hydroxyl concentration was found to be about $\text{N}/1000$ or about 6% hydrolysed. They explain the abnormal increase of equivalent conductance, observed with the higher fatty acid salts, by the formation of highly mobile colloidal anions from the fatty acid salts. To explain this rise in equivalent conductivity, they make the assumption that the

anion is a complex aggregate of a number of simple anions, each of which carries its normal charge. These several charges when distributed over the surface of the colloid are sufficient to raise the charge to a value that gives the increased mobility even though the frictional resistance is increased with the larger particle.

McBain and Salmon (7) used the conductance data in combination with indirect vapor pressure measurements to make approximate calculations of the amounts of various constituents in soap solutions. They were able to show that the particles in soap solutions and gels were aggregates of the simple soap molecules. If the solution were very dilute, then the solute was largely a molecular solution such as a solution of sodium acetate.

The colloidal theory of detergency resulted from this work on soap solutions. According to this theory, a soap solution is composed of simple molecular soap solution and charged soap particles which are aggregates of the simple units. According to Salmon (6), these soap micelles migrate toward the anode when under a potential, with a rate equal to the potassium ion. When these particles come in contact with dirt particles, which are also charged

particles, they neutralize the charges and adsorb the dirt particles thus preventing flocculation or deposition. Fall (4) states that the distinctive characteristic of soap solutions is the low surface tension imparted to the solution by the soap and that on this property depends its great power of (a) wetting surfaces, (b) dispersing and suspending small solid particles and droplets of liquids immiscible with water, and (c) lubricating surfaces and dirt particles.

If the dirt is adsorbed on a solid surface, soap solutions, because of the low surface or interfacial tensions, are able to wet both the dirt and the surface. They also lubricate the solids, making for an easy separation, probably by coating both solids with the viscous soap solution. Either mechanical agitation or the bombardment of the dirt particles by the soap micelles loosens the lubricated dirt particle. After, it is adsorbed by the particle which prevents redeposition on the solid surface. Simple rinsing removes both from the solid.

It is certain that any theory which is to be the final explanation of detergent action must consider the soap solution; the dirt, whether liquid or solid; and the surface

to be cleansed, each as a colloid. Many other theories of detergent action have been given at various times, but the colloidal theory seems to be the accepted theory at the present time.

The X-ray investigations of Thiessen and Spychaliski (9) showed that soap micelles have the structure of the crystalline neutral water free fatty acid salt. Water fills only the intercellular and capillary spaces in the soap gel. The molecules of the salts are arranged at right angles to the long axis of the rod like micelles.

METHODS OF DETERMINING DETERGENCY

McBain, Hawthorne, and King (8) developed the first quantitative method for the determination of detergent power. This is an application of Spring's method (5) in which the carbon black carried through a filter paper by the soap solution is estimated. The carbon black carried through the paper in a definite volume of solution was estimated by comparison which allowed quite some error. The quantity of carbon, and hence the detergent value, varies with the filter paper, the method and pressure of folding, and with the amount of carbon retained in the filter paper itself. It seems that this method would give

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very unsatisfactory results because of its variables.

Fall (4) evaluates detergent power of soap solutions by suspending colloid mill manganese dioxide under definite, controlled conditions and then volumetrically determines the amount in suspension. This method eliminates the difficulties of the McBain method (8) and the author claims that quantitative results can be obtained by using the method for determining manganese dioxide in pyrolusite.

The Fall method of determining detergent power was tried several times with out success. It was found impossible to secure check results in solutions of soap with a high proportion of unsaturated fatty acids.

Chapin (10) determines the relative deflocculating or detergent efficiencies by a method based on the behavior of powdered flake graphite in suspension. He states that a white crescent appears in the foam, at the junction of the solution and the foam, when the optimum concentration has been reached.

Stericker (11), White and Marden (29) and others have used measurements of surface tension against air, drop numbers and foam numbers as measures of detergency.

Stericker (11), Millard (12), Hillyer (3), Elledge and Isherwood (13), Briggs and Schmidt (14), Lenher and Buell (15), Richardson (16), and others have used measurements of interfacial tension against oils as detergent values.

Papaconstantinou (17) valued the protective action of soap solutions by measuring the gold numbers.

Stericker (11), Rhodes and Brainard (18), Snell (19), Morgan (20), and others have used direct washing with soiled cloth under controlled conditions of temperature and concentration. In these tests, the dirt was suspended in a solution of fat and oil containing solvent. The cloth was then soiled with the oil covered particles which according to Snell (19) represents the dirt most difficult to remove.

Vincent (21) states that concentrated soap solutions are good detergents because of their extremely efficient wetting and emulsifying ability.

Mullin (22) states that cleansing action increases almost as a straight line function of the pH. Rhodes and Bascom (23) show that maximum detergent effect is obtained at a pH of 10.7. They state that the detergent power of a neutral soap first increases and then decreases

as the alkalinity of the solution is increased. Also the detergent power seems to increase with the valence of the anion present.

Mikumo (24) states that washing tests indicate that detergent action of soaps runs parallel with the surface tension and interfacial tension against kerosene and is very high when the surface tension is lowest. This, he says, indicates that the active detergents in pure soap solutions are highly dispersed components, especially simple soap molecules, fatty acid ions, or very fine colloid units.

Van der Werth (25) believes that there are three dominant factors which determine cleansing power; adsorption, emulsifying power, and wetting ability. He also believes that washing tests are essential for evaluating detergents.

Many mechanisms of detergent action and many methods have been devised for the measurement of detergents action, but none of them have proven to be direct measures of this power. Washing tests performed with soiled cloth and under controlled conditions have become the most used methods of evaluating detergent power.

EXPERIMENTAL METHODS

Surface Tension

Surface tension measurements were made at 60° C. with a Findlay's surface tension apparatus. The densities of the solutions were considered to be the same as water at the same temperature. The equation (27) for relating surface tension in dynes per centimeter to capillary rise is :

$$\gamma = \frac{1}{2} \rho h d g r.$$

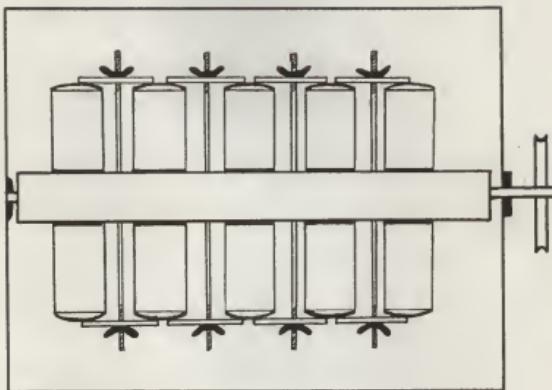
pH Value

The pH value was measured with a potentiometer. It was found that a platinum electrode would give check results in alkaline soap solutions. The equation (28) for the calculation of the pH value with a standard calomel half cell using saturated potassium chloride solution and a platinum electrode at 25° C. is: $pH = \frac{E_t - 0.2464}{0.0591}$

Detergent Power

The detergent power of the soap solutions was determined by the method outlined by the Detergents Committee Report to the Oil Chemists' Society (26) in 1931.

Figure I



Jars Arranged in Washing Machine.

Figure I represents the washing machine used in the detergent tests. This machine is similar to the Launderometer manufactured by the Atlas Devices Company, Chicago, Illinois and the Jars are Atlas E-Z Seal pint jars. The washing machine consists of a horizontal shaft geared to a motor such that it can be rotated at a speed of 40 r.p.m. It is arranged to hold one-pint jars placed

radially about the shaft with the base of the jars two inches from the center of the shaft. The temperature of 60°C. is maintained by means of water into which the jars dip during part of each revolution.

"Utica" brand sheeting, manufactured by the Utica Steam and Mohawk Valley Cotton Mills, Utica, New York, having 27 threads per inch in the warp and 25 threads per inch in the filling and free from sizing, was cut into strips about 13 inches wide. These strips were soiled by immersing in a water suspension of oil free carbon black carrying about 20 grams per liter. The carbon black used was grade "J" supplied by L. Martin Company of Philadelphia.

The strip of cloth was first wet with distilled water, then placed in the carbon suspension for a short time and then passed through the rolls of a tightly set clothes wringer. This operation is repeated until the color ceases to become deeper, then it is placed in a jar and shaken with fresh portions of distilled water until the carbon black no longer appears in the rinse water. The strip is dried at room temperature, cut into pieces about $3\frac{1}{2}$ " x 6" and sewed into bags in which 50 Monel metal balls $1/4$ inch in diameter are placed.

The detergent solutions were prepared by dissolving definite quantities of soap or soap and builder in a small volume of distilled water and then diluting to volume at 60°C. The soap and builder concentrations are expressed as per cent by weight.

Two test bags are placed in each jar with 100 cc. of the detergent solution. The jars are capped and clamped into the washing machine. The jars are rotated for twenty minutes at 40 r.p.m. and at 60°C. The solution is then poured from the jars and 100 cc. of fresh solution is added to each jar, and rotated again. After six twenty minute washings, the bags are rinsed with three successive 100 cc. portions of distilled water at 60°C. The bags are then cut open and dried in air on a glass plate.

The detergent power of the solution is determined with the use of an Ives tint photometer. The whiteness of the original soiled unwashed cloth is determined by direct comparison with a magnesia block and stated as per cent whiteness since the Ives scale has 100 divisions. The whiteness of the washed pieces is measured in the same manner and the increase in whiteness in Ives units is taken as a measure of the detergent power of the solution in which the cloth was washed.

It is admitted that this method does not take into consideration the different kinds of dirt, the different kinds of cloth, and other variables. According to Vail (26), soil of this type is the most difficult to remove from fabric and therefore it should be the type for determining detergent power.

Electrodialysis of Sodium Oleate

The soap used in all tests was Merck's "Sodium Oleate, Neutral Powder". In order to determine whether the minute traces of salts in the soap had any effect on the measured properties, a quantity of the sodium oleate was electrodialyzed against distilled water with a six volt current until the spectroscope showed only the very faintest sodium lines. The liberated fatty acid was dried to constant weight in a vacuum oven at 50°C. Soap was formed by treating the free acid with its chemical equivalent of sodium hydroxide in water solution. The detergent solutions of definite soap concentrations were made from the electrodialyzed sodium oleate solution.

EXPERIMENTAL DATA

Table I

Detergent Value, pH, and Surface Tension
of Sodium Oleate Solutions

| No. of Samples | Detergent Solution % by wt. | Increased Whiteness Ives % | pH Value | Surface Tension Dynes/cm. |
|----------------|-----------------------------|----------------------------|----------|---------------------------|
| 2 | 0.00 Na oleate | 11.6 | 8.3 | 67.1 |
| 6 | 0.01 " | 18.9 | 8.5 | 36.4 |
| 6 | 0.03 " | 21.1 | 9.7 | 27.4 |
| 6 | 0.05 " | 12.8 | 10.0 | 25.8 |
| 6 | 0.07 " | 16.2 | 10.15 | 25.3 |
| 6 | 0.10 " | 12.4 | 10.2 | 25.8 |
| 6 | 0.12 " | 15.0 | 10.1 | 24.1 |
| 6 | 0.15 " | 11.9 | 10.3 | 25.7 |
| 6 | 0.20 " | 14.1 | 10.2 | 24.9 |

Note: No. of Samples represents total number of cloth pieces washed in each solution.

Table II

Detergent Value, pH, and Surface Tension
Electrodialyzed Sodium Oleate Solutions with Caustic

| No. of Samples | Detergent Solution % by wt. | Increased Whiteness Ives % | pH Value | Surface Tension Dynes/cm. |
|----------------|-----------------------------|----------------------------|----------|---------------------------|
| 6 | 0.03 soap | 13.6 | 9.2 | 31.3 |
| 6 | 0.03 " + .0025 NaOH | 14.6 | 10.2 | 26.8 |
| 6 | 0.03 " " .005 " | 14.2 | 10.7 | 27.0 |
| 8 | 0.03 " " .01 " | 13.7 | 11.1 | 30.2 |
| 6 | 0.03 " " .015 " | 14.3 | 11.3 | 30.6 |
| 6 | 0.03 " " .02 " | 14.4 | 11.4 | 35.0 |
| 2 | 0.03 " " .03 " | 15.1 | 11.6 | 33.4 |

Table III
Detergent Value, pH, and Surface Tension
of Sodium Oleate Solutions with Builders

| No. of Samples | Detergent Solution % by wt. | Increased Whiteness Ives % | pH Value | Surface Tension Dynes/cm. |
|-------------------|-----------------------------------|----------------------------------|-------------|---------------------------------|
| 6 | 0.03 soap | 21.1 | 9.7 | 27.4 |
| 6 | 0.03 " & .005 NaOH | 18.6 | 10.7 | 30.6 |
| 6 | 0.03 " " .01 " | 17.3 | 11.0 | 31.5 |
| 6 | 0.03 " " .02 " | 15.4 | 11.4 | 31.7 |
| 2 | 0.03 " " .03 " | 13.3 | 11.6 | 31.3 |
| 6 | 0.03 " " .025 S Sil. | 17.8 | 9.7 | 26.9 |
| 6 | 0.03 " " .05 " " | 17.2 | 9.8 | 25.9 |
| 6 | 0.03 " " .075 " " | 16.7 | 9.8 | 25.9 |
| 2 | 0.03 " " .10 " " | 16.3 | 9.9 | 25.1 |
| 6 | 0.03 " " .005 M Sil. | 16.8 | 10.0 | 27.2 |
| 6 | 0.03 " " .01 " " | 16.2 | 10.4 | 26.1 |
| 6 | 0.03 " " .02 " " | 16.8 | 10.6 | 25.3 |
| 2 | 0.03 " " .03 " " | 13.8 | 10.9 | 25.1 |

Note: All silicates are products of Philadelphia
Quartz Company.

Note: S Sil. is the "S" Brand ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.86$)
M Sil. is the "Metso" Brand ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:0.97$)

DISCUSSION OF THE DATA

Table I gives the average values of the detergent power, pH value, and surface tension for solutions ranging from zero to 0.20% neutral sodium oleate by weight. Neutral sodium oleate means the compound composed of equivalents of sodium and oleate ions and does not refer to the pH values of its solutions. The pH values increase with the soap concentration except for the 0.12% and the 0.20% soap solutions. Since it is quite easy to secure check results with a hydrogen electrode in dilute alkaline soap solutions, these measurements are considered to be correct for these solutions.

The surface tensions of the neutral soap solutions decrease to approximately two fifths that of the pure water when the solution contains 0.03% soap. The values go slightly lower for the more concentrated solutions, but they are neither constant nor regularly lowered with the increased soap concentrations.

The detergent values of the solutions of neutral sodium oleate are represented numerically in the column

marked "increased whiteness, Ives per cent". The 0.03% soap solution shows the highest detergent power of any of the solutions. This value is the same as that determined by Millard (12) from interfacial tension measurements against benzene. The data shows that the 0.15% and the 0.10% soap solutions have only slightly better cleansing powers than the distilled water.

Investigators using other methods for evaluating detergent effects have found optimum soap concentrations varying widely. McBain (8) found 4.45% soap to be the optimum soap concentration for carbon suspension. Fall (4) gives from 0.20% to 0.40% soap as the concentrations which suspend manganese dioxide to the greatest extent. Rhodes and Bascom (23) use, as do many of the later workers, soap solutions of about 0.25% concentrations. Vincent (21) found that soap solutions of 0.05% to 0.10% gave emulsions which were considered to be most stable.

In actual laundry practice, it is customary to use from 0.05% to 0.10% soap solutions, which concentrations may be lessened with the addition of alkaline builders. It may be seen that a large part of the work on soap solutions has been done with soap concentrations much

greater than those necessary in actual washing operations where the soil, cloth, and solvent effects must vary very greatly.

The solutions of soap concentrations greater than 0.03% were poor cleansing agents when the cotton cloth soiled with carbon black is used to determine cleansing power. The more concentrated solutions seemed to produce such a large volume of soap suds during the washes that the mechanical action was rendered much less effective in loosening the dirt particles. The mechanical buffering action probably explains the decreased detergent action of the solutions above 0.03% soap. It must be realized that a variation of the acid character of the dirt and salts capable of rendering the soap inactive will cause a variation of the optimum soap concentrations. The work represented in this paper was performed with acid free dirt, cotton cloth, and distilled water, all of which makes for reproducible measurements.

Table II shows the detergent value, pH value, and surface tension measurements of solutions of soap and caustic, the soap having been made from free oleic acid produced in an electrodialyzing cell. It was thought, since the cleansing action is probably closely related to

the colloidal condition of the soap solution, that the traces of inorganic ions present might have some effect upon the solution properties. The sodium oleate as supplied by Merck and Company gave qualitative tests for chloride, sulfate, and potassium ions in addition to sodium. The solution after dialysis failed to give tests for chloride, sulfate, and potassium ions and gave only a very faint line for sodium in the spectroscope. This indicates that the inorganic ions were very materially reduced in concentration.

The pH value of the soap solution without caustic is lower than the value for a 0.03% neutral sodium oleate solution. Probably the method by which the soap was prepared accounts for this low alkalinity. The pH of the solutions increases with the increased caustic concentrations while the surface tension reaches a minimum with the soap solution containing 0.005% caustic. The values for detergent effect are low and show no definite tendency, but give a maximum value with 0.03% caustic.

Table III gives the measured values for neutral sodium oleate solutions to which caustic and two different sodium silicates were added. The silicates were included in the investigation, not in an effort to determine the

value of sodium silicate as a detergent, but to produce alkali by hydrolysis. Caustic and salts which produce alkali by hydrolysis are common additions to commercial soaps. These alkalis improve the detergent effect of soaps in so far as they are able to neutralize acidic dirt and prevent the formation of insoluble soap particles.

An examination of the data will show that with caustic as the builder, the detergent power decreases while the pH value and the surface tension increases as the builder is increased in concentration. With α silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.86$), the detergent power and the surface tension decrease while the pH value increases slightly. With M silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:0.97$), the pH value increases and the surface tension decreases while the detergent power seems to have no definite tendency.

It is generally believed that soap solutions are composed of an equilibrium mixture of simple soap molecules, the products of ionization and of hydrolysis, and colloidal soap particles. According to the theory of colloidal detergency, these colloidal soap particles or ionic micelles are responsible for most of the cleansing effect of soap solutions. Since hydroxyl and alkali metal ions are formed by the soap hydrolysis and ionization, the addition of an

alkali should cause a shift in the equilibrium to give more soap molecules and more colloidal soap particles. The point at which the detergent effect is a maximum, according to Rhodes and Bascom (23), is 10.7 pH. This should mean that the colloidal properties of the soap solution are at a maximum at this alkalinity. Fall (4) states that nothing can take the place of soap itself; that if builders are added, any cleansing action which they show is shown because they are taking the place of a certain amount of soap of greater detergent efficiency.

Any soap solution, according to Snell (19), having a pH of 10.2 or less is acid to soap. As such, one would expect the detergent action to be low since there is a large tendency to form insoluble acid soap particles. Throughout this work, maximum detergent effects were produced in solutions whose pH value was below 10. Apparently acidic soap solutions have real detergent powers.

CONCLUSIONS

Measurements on dilute solutions of sodium oleate and on sodium oleate solutions to which some of the common alkaline builders have been added, do not show any direct relationship between the detergent power as measured, the pH value, and the surface tension. Consequently, it may be concluded that in the range studied, the detergent effect is neither proportional to the pH nor to the surface tension lowering of the solutions.

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